TECHNICAL REPORT 4042

DIFFERENTIAL THERMAL ANALYSIS

OF

PRIMARY EXPLOSIVES

A MODIFIED TECHNIQUE

R. J. GRAYBUSH
F. G. MAY
A. C. FORSYTHE

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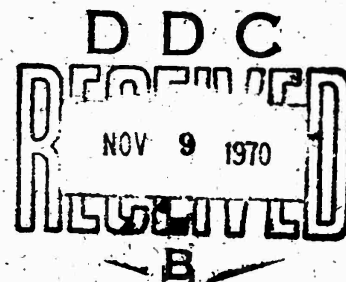
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PICATINNY ARSENAL

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DIFFERENTIAL THERMAL ANALYSIS OF PRIMARY EXPLOSIVES

A MODIFIED TECHNIQUE

by

R. J. Graybush
F. G. May*
A. C. Forsyth

September 1970

Feltman Research Laboratories
Picatinny Arsenal
Dover, N. J.

*Guest scientist from Defense Standards Laboratories, Department of Supply, Melbourne, Australia, at present at Explosives Laboratory, Feltman Research Laboratories, Picatinny Arsenal

ACKNOWLEDGMENT

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OBJECT

To develop a thermal-analytical procedure capable of evaluating initiatory explosives.

ABSTRACT

The usefulness of DTA (differential thermal analysis) in the study of primary explosives has been diminished by the tendency of samples to detonate in the course of the analysis. This report describes modifications made to the remote cell used in conjunction with a du Pont 900 DTA, and which minimize the probability of detonation. Using lead azide to evaluate the technique, it is shown that complete curves of the exothermic decomposition

$$PbN_6 \rightarrow Pb + 3N_2$$

are obtained reproducibly. The endotherm in the curve corresponding to the fusion of the lead product serves as confirmation of the reaction, and it is employed as an internal temperature calibration. Illustrations are given to show extensions of the system to other initiating explosives of military interest, i.e., lead styphnate, mercury fulminate, and potassium dinitro benzfuroxan (KDNBF).

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INTRODUCTION

In recent years thermal analysis, and especially DTA, has been widely accepted as a useful tool in research investigations and product control of explosives (Ref 1, 2, 3, 4). Most of the literature involves applications related to secondary explosives, since these are less liable to detonate in the sample holder. This danger being absent, or at least greatly diminished, the technique has found wide use in the study of reaction kinetics (Ref 5, 6, 7) and phase transformation phenomena (Ref 8, 9, 10).

A survey of the literature relating the use of this method to the more sensitive primary explosives (Ref 4, 11, 12, 13) is much less rewarding. When these samples are examined using routine methods of DTA, a high incidence of detonations can be expected. Even though sample size can be reduced to a point where there is little risk of instrument damage, this is an undesirable situation, since the amount of significant data which can be extracted from such a curve is minimal. If detonation is avoided, e.g., by the use of very slow heating rates in an inert atmosphere, the ensuing reaction may be very difficult to characterize. For lead azide, decomposition can result in the formation of a mixture of various oxides of lead. Since this reaction is strongly influenced by trace quantities of oxygen, the proportion of these oxides in the mixture is, however, not constant nor can it be predicted. Consequently, reproducibility is just as uncertain as in the cases of actual sample detonation. In a critical study of the thermal properties of a material it is of prime importance that the reaction mechanism be well defined. It is the opinion of the authors that previous investigators have not paid sufficient attention to this point.

The decomposition of lead azide

$$PbN_6 \rightarrow Pb + 3N_2$$
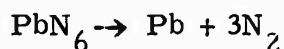
was selected as the principal reaction for study because it is known to occur in the detonation process (Ref 14), can be easily characterized, and is definitely reproducible. The study of the thermal processes involved in the reaction is of much relevance to an understanding of the explosive behavior of lead azide when it is subjected to stimuli involving heating of the material.

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This report describes modifications which were made to the remote cell of a du Pont 900 DTA in order to attain this objective. The versatility of the method in its application to other primary explosives is demonstrated.

Remote-Cell Modifications

A typical remote cell 900 DTA as currently supplied by E. I. du Pont is shown in Figure 1. It differs from earlier models in that the heating block has been raised and is separated from the thermocouple connections by a large insulating disk of asbestos. Experience with earlier designs of that cell had shown the imperative importance of protecting these connections from exposure to stray thermal currents. The need to protect samples from oxidizing environments necessitated the cell being pumped down to a vacuum of 10^{-6} torr, which, in turn, required removal of the porous disk and redesign of the support. It also was necessary to seal the electrical connectors, relocate the gas inlets, and modify the base plate and locking clamps.

The modified cell (Fig 2, 3) was mounted on a new brass plate, into which four holes were drilled to accommodate vacuum-tight cartridge bushings A-2622, supplied by Glass Tite Industry, Providence, Rhode Island, which were in turn soldered into the plate. The pins from the original plug were soldered into the new bushings to adapt them to existing thermocouple and heater connections. The new heating block holder and support consisted of a single unit fabricated from heavy-walled glass and coated with silver. The thermocouple connections were further protected by shielding them with glass tubing. Evacuation and gas flow were effected through two pressure-vacuum stopcocks attached to the top of the pyrex dome. The pyrex dome was made vacuum-tight by fastening it to the base with a ring seal and a metal collar.

DTA Procedures

The samples investigated were in the form of fine crystalline powders. When using standard 2 mm-diameter capillary tubes, the sample weight was approximately 0.5 mg, in 4 mm-tubes a maximum of 2.5 mg could be used. The weight could be increased to 5 mg if the sample were diluted with an equal volume of glass beads (Ref 15). Reference and heater-control tubes were filled with glass beads to the same height as the sample tube. In all cases materials were

compacted by mild tapping. The cell was evacuated for several minutes at 10^{-6} tor: before backfilling and purging with dried helium gas. A flow rate of 400 cc/min of helium gas was maintained throughout the experiment. Heating rates of up to 10°C/min and maximum instrument sensitivity of 0.1°C/inch could be used. Standard chromel alumel thermocouples were employed.

Fisher Scientific "Thermetic" standards and high-purity lead (99.999%) supplied by Electronic Space Products, Inc., Los Angeles, California, were applied for instrument calibration. Lead azide of high purity was prepared by reaction of lead nitrite with hydrozoic acid (Ref 16). Other explosive samples were of military-grade stock.

RESULTS AND DISCUSSION

Figure 4 shows curves obtained for the melting point standards: napthalene, mp 80.20°C; benzoic acid, mp 122.33°C; 2- chloroanthroquinone, mp 209.3°C; and pure lead, mp 327.5°C. These curves were found to be consistant with those obtained by using standard techniques.

Curves for lead azide are shown in Figures 5 and 6. Two unacceptable curves, Figure 5a, sample detonation, and Figure 5b, sample oxidation, also are shown. It is readily evident that very little information can be derived from the curves in which detonation occurred; also, the presence of trace amounts of oxygen causes nonreproducible distortion of the decomposition exotherm. Depending on oxygen concentration, the distortion may range from gross deformation and extended tailing of the peak to merely a moderate reduction in the peak area when only extremely minute traces of oxygen are present. When lead azide specimens were evacuated to varying pressures before backfilling and purging with helium, it was found that the exotherm peak area increased inversely in relation to pressure. This treatment did not influence either the onset or peak temperature of the exotherm. Figure 6a shows decomposition of high-purity lead azide to metallic lead as obtained in the modified system. Features of importance are the decomposition exotherm in the region of $288-310^{\circ}$C and the lead fusion endotherm at 318°C. Subsequent cooling of the sample gives the exothermic solidification of lead supercooled to 315°C. It will be noted that the lead formed as a reaction product melts at a lower temperature than that normally expected for lead; which at this time is believed to result from the high flow rate of helium gas. This lead melting peak serves a double purpose: It confirms the products

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of reaction, and it provides an internal calibration standard for normalization of lead azide decomposition temperatures (Table 1). The average deviation of the lead fusion temperature was ± 1.7°C. This gave decomposition data, with deviations of ± 0.6% at the average onset temperature of 287°C, and ± 0.4% at the average peak temperature of 304°C. The values in Table 1 were obtained from curves using various instrument settings and sample sizes. Greater accuracy could be obtained if these parameters were held constant. From Table 1 it can be seen that considerable flexibility in the choice of instrument settings and sample configurations is possible. It was found essential to provide a rapid heat distributor in contact with the sample in order to prevent detonation and provide controlled decomposition. Consequently, helium with its high thermal conductivity was the preferred carrier gas. When sample size was increased to the point where helium gas alone was not sufficient, dilution of the sample with glass beads, commonly used for reference material, provided a heat sink (Fig 6b). This use of glass beads did not affect the peak shape.

From another study (Ref 17) it was known that lead azide prepared in the presence of various dopants has related defect structure. Figure 7 gives curves for ferric halide-doped lead azide. Work is in progress to interpret these results in terms of the observed ESR (electron spin resonance) phenomena (Ref 15).

Figure 8 shows the extension of the method to several other initiatory compounds. In all instances complete curves are obtained, and it appears that the method could equally be applied to any other sensitive material.

Efforts are currently being made to modify the accessory du Pont 950 T.G. apparatus so as to permit equivalent thermogravimetric data to be obtained.

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TABLE 1

Results of thermal decomposition of lead azide under various experimental conditions

T (onset) (°C)	T (max) (°C)	MP Lead (°C)	Sample Weight (mg)	ΔT Setting (°C/in.)	Glass Beads	Size of Capillary Tube (mm)
287	305	317	2.4	0.5	No	4
289	305	316	2.6	0.5	No	4
288	305	320	1.1	0.2	No	4
293	305	320	1.0	0.2	No	4
294	306	321	0.8	0.2	No	4
290	304	320	0.5	0.2	No	4
288	304	320	0.4	0.2	No	2
290	304	316	0.4	0.2	No	2
287	302	316	0.5	0.2	No	2
290	303	320	0.3	0.2	No	2
287	302	320	0.3	0.1	No	2
288	300	316	3.0	0.5	Yes	2

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Fig 1   Remote cell 900 as supplied by E. I. du Pont

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Fig 2   Modified remote cell

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THERMOCOUPLES
IIOV A.C. WIRE
PYREX DOME
HEATER HOLDER & SUPPORT
HEATING BLOCK
HEATER

CLAMPING SCREWS

ELECTRICAL FEED THROUGHS
RING CLAMP

CABLE TO INSTRUMENT

170MM
45 MM
38MM
72MM

VACUUM
HELIUM

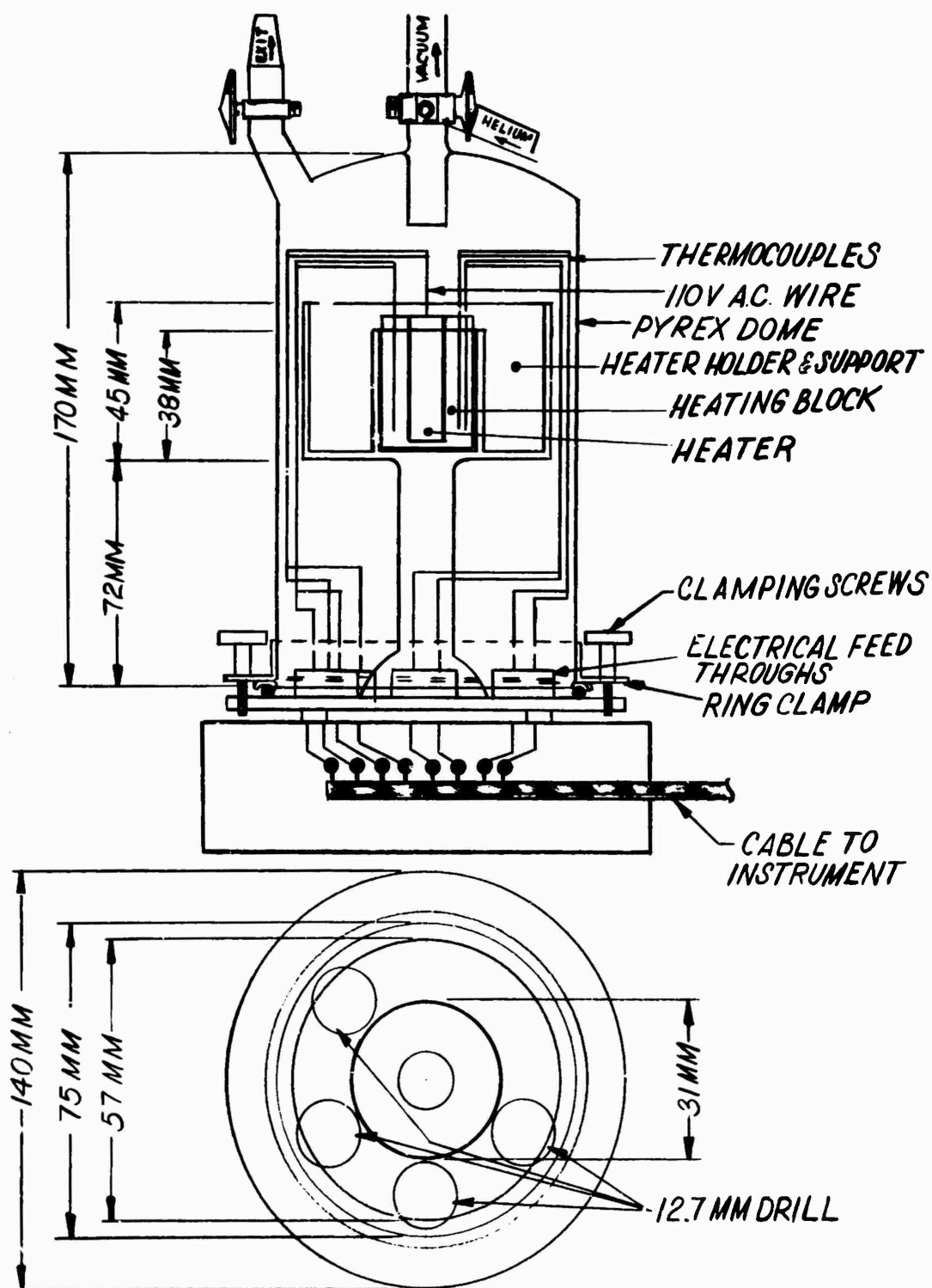140MM
75 MM
57 MM
31 MM

12.7 MM DRILL

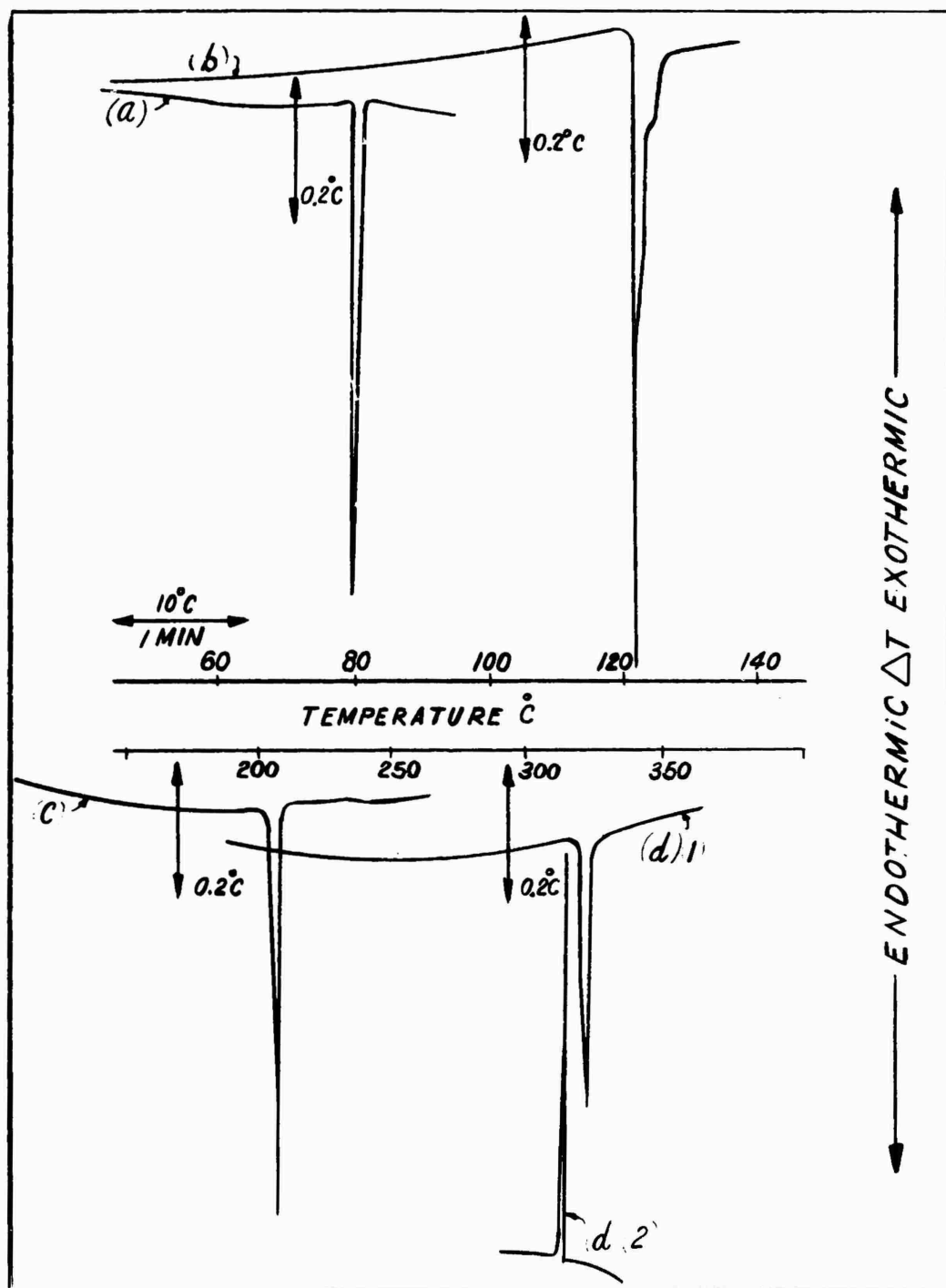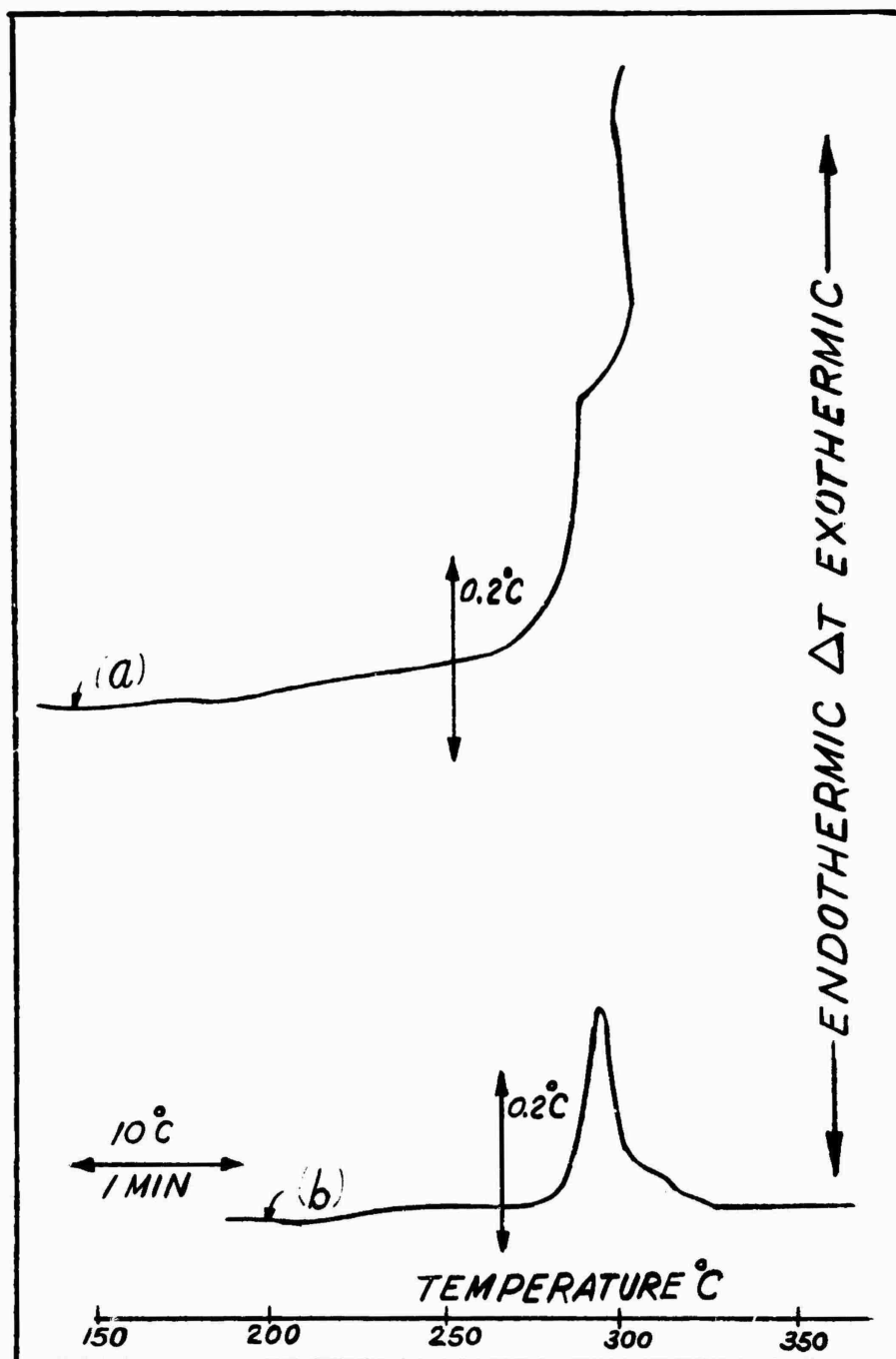FIG 3   SCHEMATIC DIAGRAM OF COMPONENTS IN THE MODIFIED REMOTE D T A CELL

FIG 4   DTA CURVES FOR CALIBRATION STANDARDS USING MODIFIED REMOTE CELL
(a) NAPTHALENE (b) BENZOIC ACID (c) CHLOROANTHROQUINONE
(d)(1) LEAD MELTING
(d)(2) LEAD SOLIDIFICATION

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DTA CURVES FOR LEAD AZIDE
(a) SAMPLE DETONATED
(b) SAMPLE DECOMPOSED TO FORM OXIDES
OF LEAD

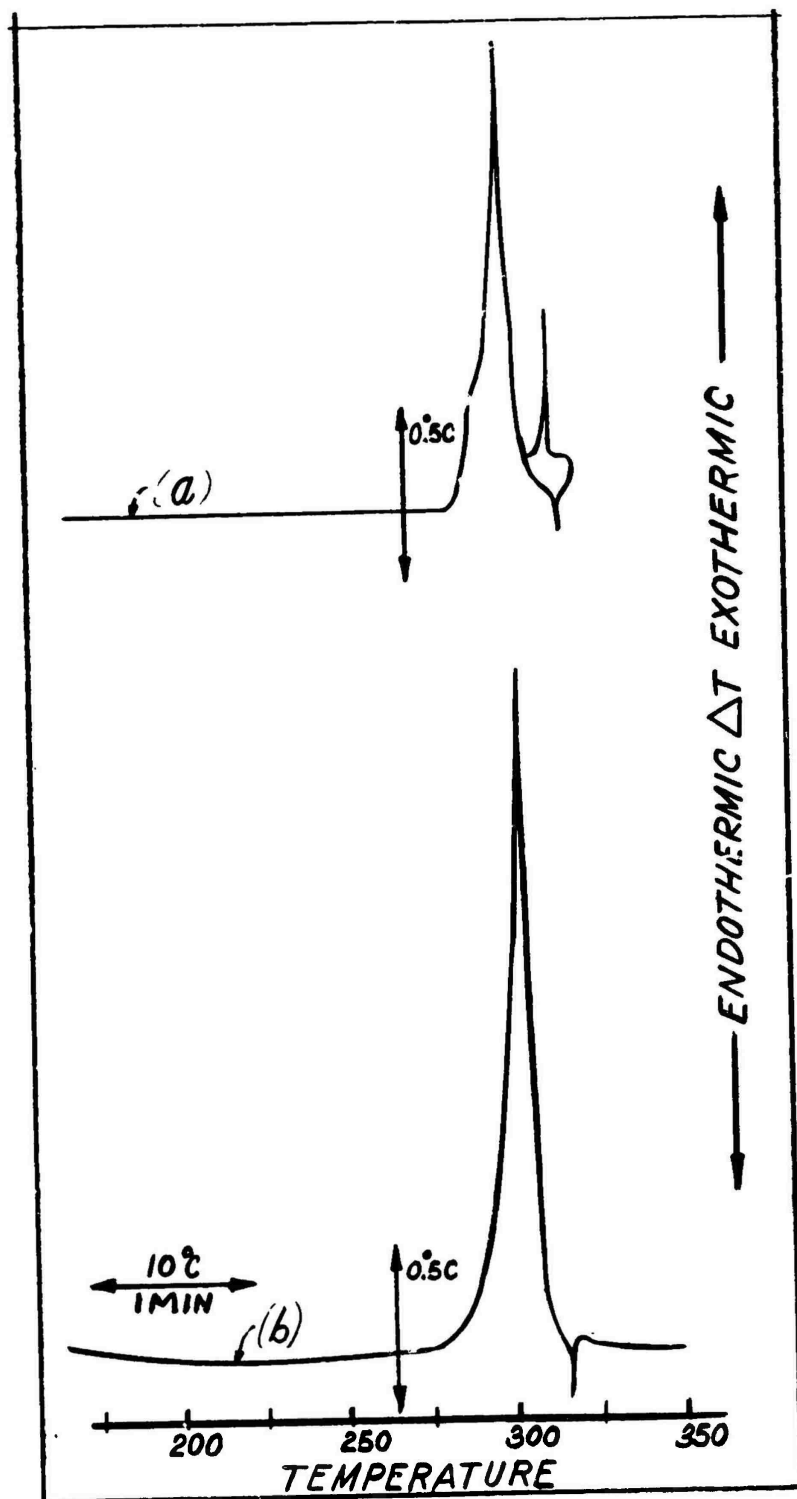FIG 5

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FIG 6   DTA CURVES FOR LEAD AZIDE USING MODIFIED
         REMOTE CELL
      (a)_ 2.6 MG LEAD AZIDE.
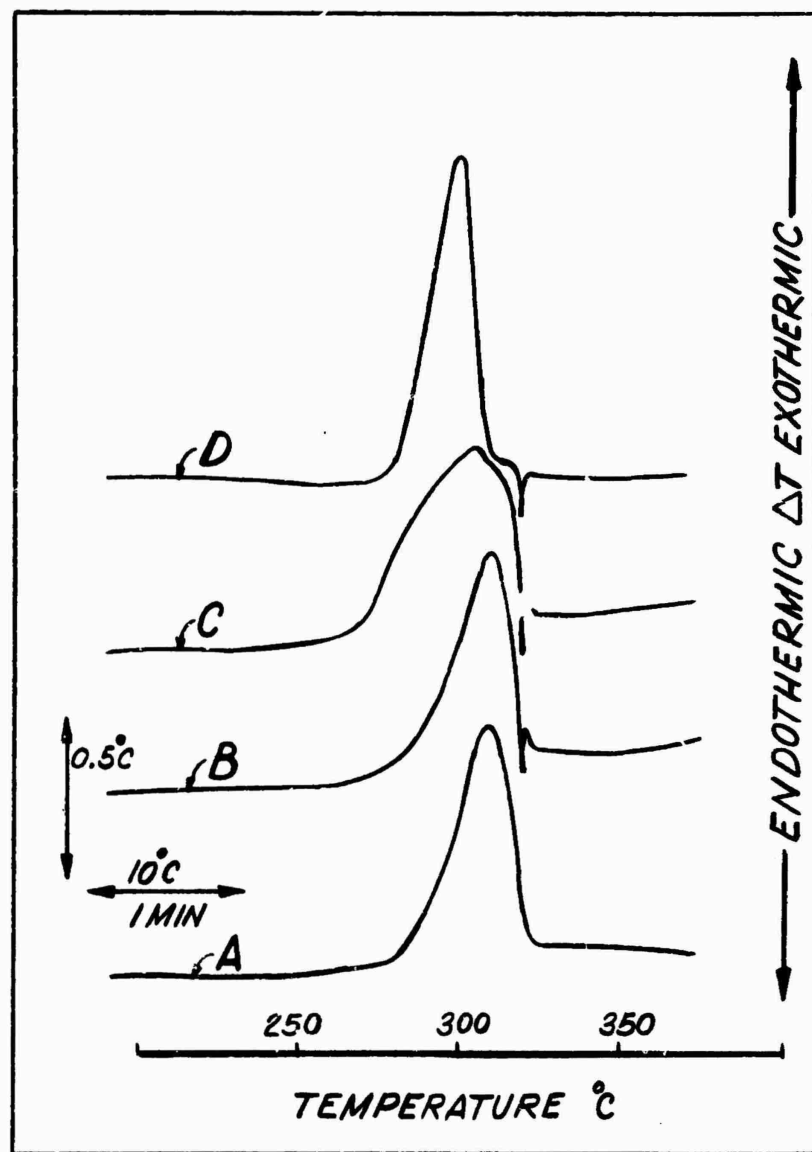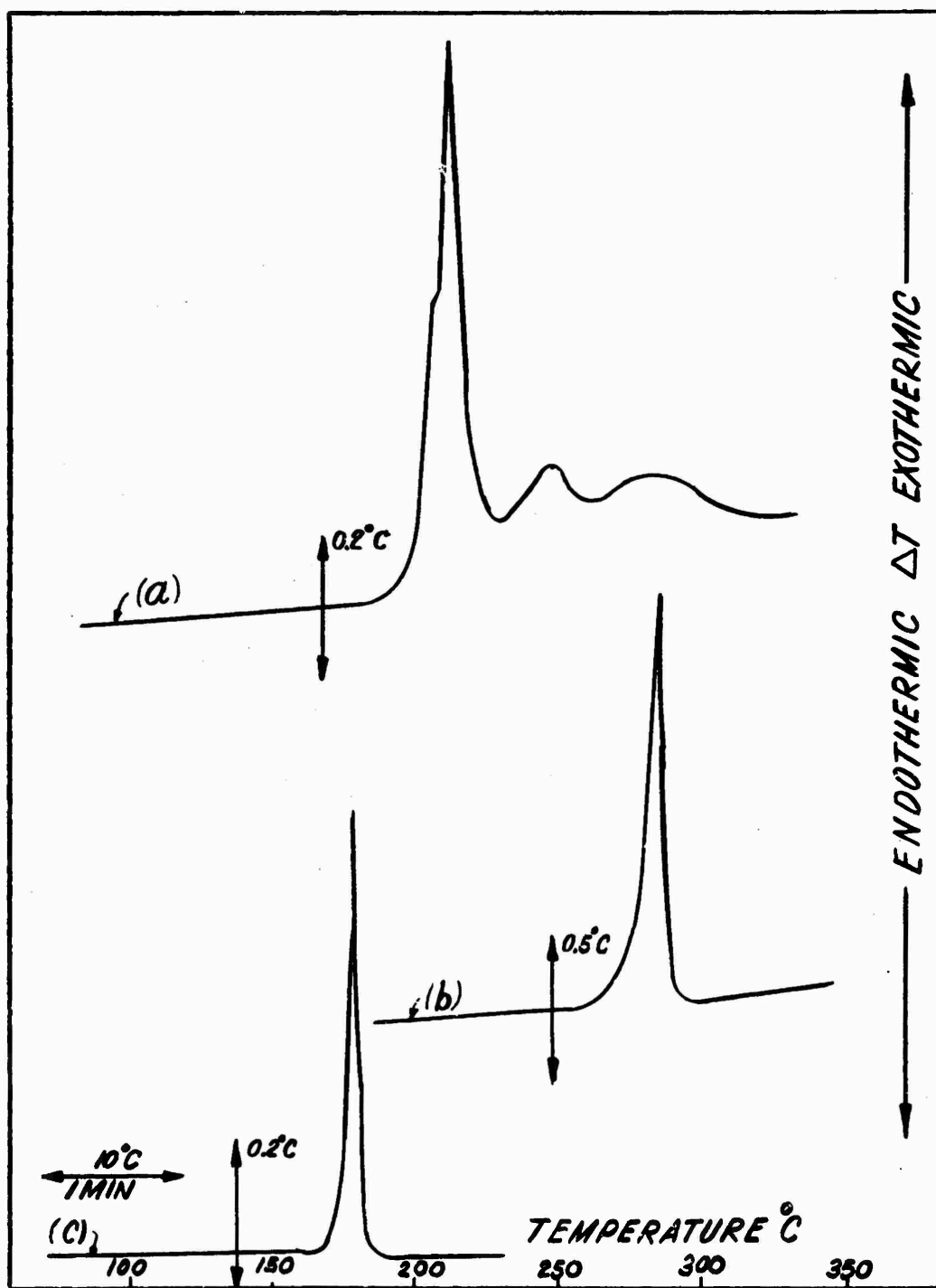   (b)_ 3.1 MG LEAD AZIDE DILUTED WITH GLASS BEADS

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FIG 7   DTA CURVES FOR IRON DOPED LEAD AZIDE
(A) $Pb\ N_6 + Fe\ F_3$ (C) $Pb\ N_6 + Fe\ Br_3$
(B) $Pb\ N_6 + Fe\ Cl_3$ (D) $Pb\ N_6 + Fe\ I_3$

ENDOTHERMIC ◄——— ΔT ———► EXOTHERMIC

0.2°C

ƒ (a)

0.5°C

ƒ (b)

10°C
1MIN

0.2C

(C)

0.2C

TEMPERATURE °C

100   150   200   250   300   350

DTA CURVES FOR OTHER PRIMARY EXPLOSIVES
(a) POTASSIUM DINITROBENZFURAN (KDNBF)
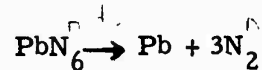(b) LEAD STYPHNATE
(c) MERCURY FULMINATE

FIG8

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R. J. Graybush
F. G. May
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13. ABSTRACT

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are obtained reproducibly. The endotherm in the curve corresponding to the fusion of the lead product serves as confirmation of the reaction, and it is employed as an internal temperature calibration. Illustrations are given to show extensions of the system to other initiating explosives of military interest, i.e., lead styphnate, mercury fulminate, and potassium dinitro benzfuroxan (KDNBF).

DD FORM **1473** REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Initiatory explosives						
Lead styphnate						
Mercury fulminate						
Potassium dinotro benzfuroxan						
Modifications to remote cell du Pont 900 DTA						
Reaction kinetics						
Phase transformation phenomena						
Secondary explosives						
Lead azide						
Glass beads						
Helium gas						
Ferric halide-doped lead azide						
Electron spin resonance						
Differential thermal analysis						